

PROPERTIES OF INDUSTRIAL SILICA SOL AND POSSIBLE MODIFICATION FOR MANUFACTURE OF ALUMINOSILICATE MATERIALS

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The properties of industrial silica sol, such as the average size and the size distribution of the particles, are examined. It is shown that separation methods (filtration and centrifuging) influence these properties of silica sol.

Key words: silica sol, particle, diameter, histogram.

Silica sol is one of the main components used in the sol-gel synthesis of ceramic materials containing mullite [1–4]. Silica sols are obtained by hydrolysis of silicon alkoxides, for example, tetraethoxyorthosilicate (TEOS), followed by polycondensation of the silicic acid formed [5, 6]. The properties of the sols obtained depend on the pH of the acids or alkali used for hydrolysis, the presence of electrolytes and organic impurities as well as other conditions of synthesis [5]. Alkaline sols, whose disperse phase is represented by spherical particles, are often used to prepare mullite ceramic. The quality of the intermediate products and final material depends on the particle size of the alkaline silica sol. Aside from the particle size, the content of alkali metals, which promote the formation of α -cristobalite during heat-treatment, plays an important role in the production of mullite ceramic [7]. Domestic producers used sodium hydroxide to obtain alkaline sols, as a result of which the silica sol becomes inapplicable for the production of mullite-based materials.

A technology for producing ammonia-stabilized silica sols was developed at the Scientific-Research Institute of Chemical Reagents and Ultrapure Chemical Substances (IREA) and has been implemented at the Miass Engineering Works, where production is functioning as of this moment. However, the particle size distribution (the variation factor V_{var}) of this silica sol and average particle diameter d_{av} vary from batch to batch, which makes it impossible to obtain materials with stable mechanical characteristics. The difference in the average diameter of the particles from batch to batch can reach a factor of 3 (Fig. 1). This is due to variations in the purity of the initial component TEOS.

As a result of this inconstancy of the particle size the phase composition of the ceramic materials as a whole varies, the material becomes nonuniform, the shrinkage of the material varies over the volume and defects, even including fracture of the material, appear.

The basic conditions for obtaining silica sol with the required quality are purity of the initial component (TEOS) and strict observance of the parameters of the fabrication process. Only the producer of the silica sol can solve these problems directly.

Since silica sol is an expensive component, for the user it is desirable to modify the rejected batches to the required particle size (< 20 nm).

Membrane filtration or ultrafiltration is often used to concentrate sols [6, 8, 9]. This method has been used since the 1970s and can be used not only to increase the SiO_2 mass fraction but also to separate the large sol particles, i.e., to decrease the particle size.

Ultrafiltration through polymer and ceramic membranes with pore size ranging from 300 μm to 50 nm was used in our research to decrease the particle size in order to reduce the average particle size of the concentrated industrial sol (concentration $C_{\text{SiO}_2} = 26.5 \text{ wt.\%}$).

It was found that membrane filtration is impracticable through polymer (capron, polysulfone) and ceramic (SiC , Al_2O_3) membranes because sol particles are sorbed on the surface of the filters and blobs of gel form, causing the filtration process to stop completely. For this reason, the results of investigations of the applicability of filtration through macroporous filters and centrifuging as methods of modifying the particle size of silica sols are presented in the present article.

Light scattering was used to evaluate the quality of the sols according to the change in their optical density D . Trans-

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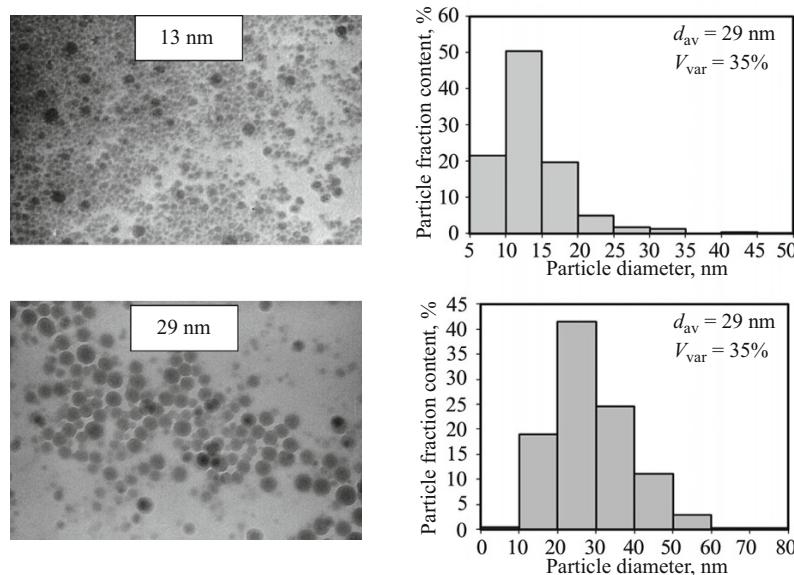


Fig. 1. Images of particles (TEM, $\times 100,000$) and histograms of the particle size distribution for different batches of silica sols.

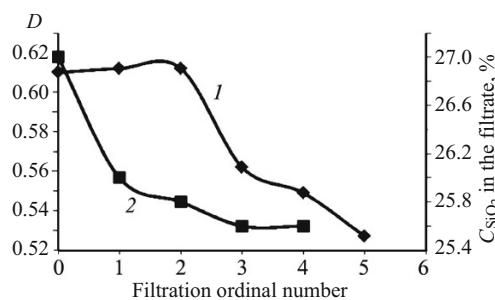


Fig. 2. Change in the optical density D (at 325 nm) (1) and silica-sol mass fraction C_{SiO_2} in the filtrate (2) with repeated filtration through a cascade of filters consisting of cellulose fibers.

mission electron microscopy (TEM) was used to determine the average particle size and to construct histograms of the particle size distribution.

First Method. This is filtration through a cascade of successive cellulose filters ($5 \rightarrow 3 \rightarrow 1 \mu\text{m}$), whose pores are

TABLE 1. Optical Density of a Silica Sol Solution (3.075 mm cell)

λ, nm	Optical density after filtration*				
	initial	1st – 2nd	3rd	4th	5th
325	0.472	0.473	0.454	0.436	0.430
364	0.610	0.612	0.562	0.549	0.527
400	0.433	0.437	0.395	0.377	0.360
440	0.306	0.311	0.276	0.257	0.245
490	0.209	0.213	0.185	0.170	0.158
540	0.151	0.155	0.132	0.114	0.109
590	0.110	0.115	0.097	0.079	0.076
670	0.073	0.071	0.059	0.049	0.047

* Each filtration goes through a cascade of filters: $5 \rightarrow 3 \rightarrow 1 \mu\text{m}$.

much larger than the sol particles. The sol sample was passed repeatedly through the filter cascade.

After the first two filtrations no changes in the optical density were observed at the wavelength $\lambda = 325 \text{ nm}$, while at $\lambda = 640 \text{ nm}$ the optical density decreased by 20%. A reduction of the silica mass fraction C_{SiO_2} in the filtrate was also observed. These results show that the large SiO_2 fraction in the filtrate decreases at the initial stage of filtration.

The subsequent reduction of the optical density at all wavelengths as well as of the mass fraction of the silica sol shows that particles of the sol settled on the filter material (Table 1, Fig. 2). A reduction of the filtration rate by more than a factor of 2 was observed at the same time, and filtration stopped completely at the fifth pass of the silica sol solution into the filtration setup. A significant amount of gel was found on the first filter ($5 \mu\text{m}$); there was no gel on subsequent filters (3 and $1 \mu\text{m}$). Since the size of the pores in a filter is much greater (by a factor 100) than the diameter of the particles, we can talk about sorption of particles on the surface of the filter fibers.

A subsequent TEM examination of the silica-sol samples showed that the particle size in the initial sol sample and in the filtrate is practically identical and the character of the histogram of the particle size distribution did not change (Fig. 3), which shows that sol particles of different sizes are sorbed at the same time on the filter surface. Therefore, we can talk about the desirability of single-stage filtration of sol through filters comprised of artificial fibers. With repeated filtration silica sol particles are sorbed on SiO_2 particles that have already been sorbed.

Second Method. This is separation in a centrifugal field.

The separation was performed in a laboratory centrifuge with centrifugal acceleration $g = 17,500 \text{ m/sec}^2$ until the solid phase was isolated from the silica-sol solution. The

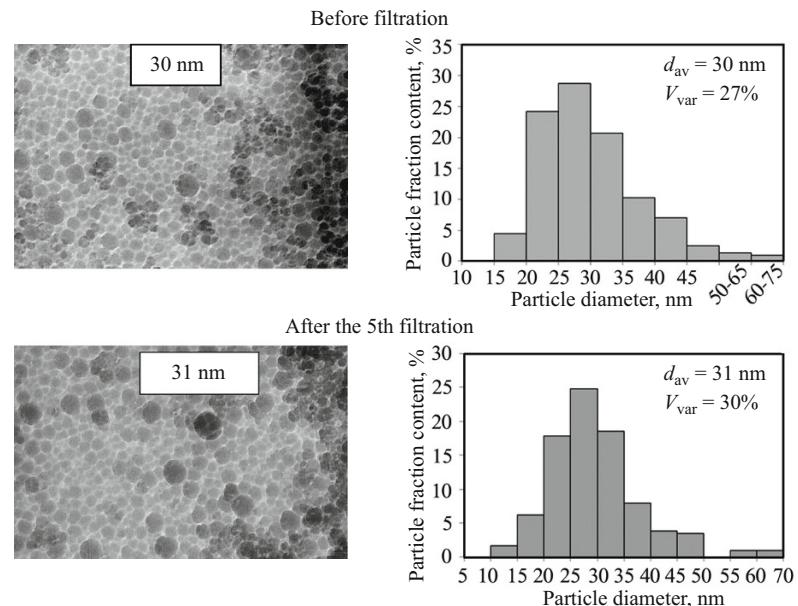


Fig. 3. Image of silica sol particles (TEM, $\times 100000$) and histograms of their particle size distribution before and after five-fold filtration through a cascade of filters comprised of cellulose fibers.

changes in the optical density and C_{SiO_2} in the sol are presented in Table 2. An investigation of the TEM specimens showed that with the exception of the fraction 60–70 nm the particle size distribution remained the same (Fig. 4), and the optical density D changed because the SiO_2 mass fraction decreased. On the basis of these results it can be supposed that particles of different sizes are separated simultaneously from the silica sol solution. Thus, the standard laboratory centrifuges are inapplicable for separating large particles (20–60 nm).

Samples of silica sol and the precipitate settling under gravity during storage ($g = 9.81 \text{ m/sec}^2$) were studied for comparison.

It was found that the size of the SiO_2 particles and the histogram of the size distribution of the particles in the precipitate and the solution are identical (Fig. 5). This allows us to talk about the fact that co-precipitation of particles of different sizes from the silicate sol solution is observed.

A concentrated silica sol was used to change the particle size in the methods described above. It is known that in order for the ultrafiltration process to be efficient it is best to use dilute sol solutions.

This investigation of the dependence of the ultrafiltration rate and particle size in the filtrate on the sol concentration (dilution ratio (DR)) has shown that as the DR of the silica sol increases to 1 : 100 the filtration rate increases 15-fold and the average diameter of the particles and the coefficient of variation V_{var} decrease by 4 nm and 10%, respectively.

Evidently, the reduction of the particle size is very small. In addition, dilution of the sol is technologically uneconomical because a large quantity of water must be removed in the process of concentrating the forming solutions.

In summary, filtration, membrane filtration, centrifuging and settling are inapplicable for controlling the particle size

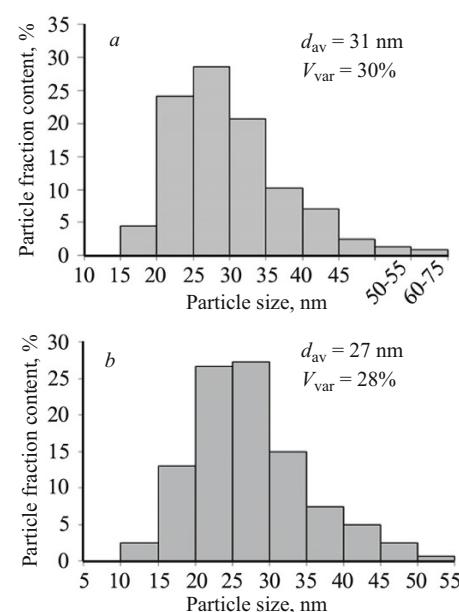


Fig. 4. Histograms of the size distribution of silica sol particles before (a) and after (b) centrifuging.

in ready (factory-made) silica sols. Silica sols with a strictly prescribed (required) particle size are required in order to

TABLE 2. Optical Density D and C_{SiO_2} Mass Fraction during Centrifuging (670 nm, 20.075 mm cell)

Index	Centrifuging			$\Delta D, \%$
	initial	1st	2nd	
D (at 670 nm)	0.360	0.245	0.208	0.196
$C_{\text{SiO}_2}, \%$	26.5	25.9	24.6	23.4

45.5

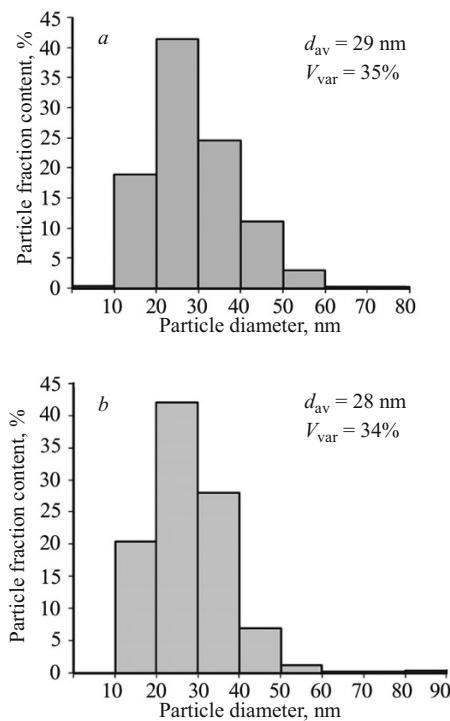


Fig. 5. Histograms of the size distribution of silica sol particles before (a) and after (b) centrifuging.

fabricate technical ceramics with definite prescribed properties. For this reason, it is necessary to take account of the fact that deviations from the technological parameters during the fabrication of silica sols and the raw material used result in deviations of the particle sizes of silica sol from the prescribed values. It would be extremely difficult to adjust the size range of the silica sol particles by accessible means un-

der factory conditions for the fabrication of heat-shielding materials.

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